Chapter 3 – The Second and Third Laws of Thermodynamics


A. The direction of spontaneous change.

1. Spontaneous process = one that does not require work to bring it about.

E.g. Expansion of a gas against a lower pressure.

The reverse does not happen naturally (i.e., spontaneously).

E.g. Heat flows spontaneously from hot to cold, but not the other direction.

E.g. the kinetic energy of the bouncing ball is slowly but inexorably dissipated into the thermal motion of atoms in the floor, but never has the reverse been observed.
E.g. The process on the right, in which all the heat flowing from the hot source into the engine can be converted to work, is not possible.

Question: What determines spontaneity? What determines the irreversible direction of these and other processes?

Verbal definition: **Spontaneous direction of change leads to increased dispersal of energy in the system plus surroundings.**

Can we quantify this?


$$\Delta S_{\text{tot}} > 0$$

The total entropy of all parts of a total system (isolated system) increases in a spontaneous change.

3. Contrast with First Law.

- First Law describes what processes are permissible as far as conservation of energy is concerned.
- Second Law describes which of these permissible processes are likely to occur, that is, which can occur spontaneously.

4. What is Entropy, review microscopic or statistical definition.

$$S = k_B \ln W$$

$k_B$ = Boltzmann constant = gas constant for a single molecule rather than a mole.

$$k_B = \frac{R}{N_A} = 1.381 \times 10^{-23} \text{ J K}^{-1}$$

$W$ = the number of different ways a system of atoms and molecules can be arranged and still be in the same thermodynamic state.
E.g. System of N particles that can have either spin up or spin down.

\[ N_+ = \# \text{ up} \quad N_- = \# \text{ down} \quad N = N_+ + N_- \]

\[ W(N_+,N_-) = \# \text{ of ways of arranging } N_+ \text{ with spin up, etc.} \]

\[ = \frac{N!}{N_+!N_-!} \]

\[ W(0,100) = 1 \text{ way} \]
\[ W(100,0) = 1 \text{ way} \]
\[ W(50,50) = \text{ huge } \# \text{ of ways } \sim 10^{30} \]

\[ S(50,50) = k_B \text{ 100 ln } 2 \quad \text{(maximum entropy)} \]

Box of coins will spontaneously tend toward state of approximately the same number of ups and downs.

Conclusion: *Isolated system will tend spontaneously toward a state containing the largest number of available microstates (molecular arrangements) at the fixed total energy.*

Remember:

\[ S = \frac{U - U(0)}{T} + k_B \ln Q \]

5. **What is Entropy, thermodynamic or macroscopic definition?**

Since entropy is about energy dispersal, and that in turn has a lot to do with thermal energy (disorganized), it is not surprising that changes in entropy are given by:

\[ dS = \frac{dq_{\text{rev}}}{T} \]

or

\[ \Delta S = \int_{1}^{2} \frac{dq_{\text{rev}}}{T} \quad \text{(path integral along the reversible path between two thermodynamic states.)} \]
i.e., Entropy change $\Delta S$ to go from state 1 to 2 by ANY path is the integral of $dq/T$ along the reversible path that connects those two states.

Problem: Calculate $\Delta S$ when ideal gas expands isothermally from $V_1$ to $V_2$, whether reversibly or irreversibly.

Strategy: construct the reversible pathway for this process and integrate $dq_{\text{rev}}/T$ even if the process were to happen irreversibly.

$$\Delta S = \int_{1}^{2} \frac{dq_{\text{rev}}}{T}$$

reversible isothermal expansion

$$dw = -pdV$$
$$= -(nRT/V)dV$$
$$dq = -dw \text{ since } dU = 0$$
$$dq = +(nRT/V)dV$$

$$\Delta S = \int_{1}^{2} \frac{(nR)}{V}dV$$

$$\Delta S = nR \ln \frac{V_2}{V_1}$$

(conditions here: revers or irrev/isothermal/perfect gas)

Note: for $\Delta S$ to be $>0$, $V_2$ must be $> V_1$

Work example: Calculate the entropy change when one mole of ideal gas expands into a vacuum and doubles its volume at 298 K. (In other words, this is an irreversible process)

We know that \( dS_{\text{tot}} > 0 \) in spontaneous change, or

\[
dS + dS' > 0
\]

A reversible change is a special idealized limiting case in which

\[
dS + dS' = 0, \text{ or } dS = -dS'
\]

In a reversible process the entropy change in system is exactly compensated by change in surroundings.

But in general:

\[
dS \geq -dS'
\]

\( \uparrow \)equality is for reversible case

so that \( dS_{\text{tot}} \geq 0 \).

We can calculate the entropy change in the surroundings as follows:

Since surroundings are the entire universe, it is a reservoir of constant volume, so energy \( dq_{\text{surr}} \) supplied to it as heat = \( dU_{\text{surr}} \).

So state function \( dU_{\text{surr}} = dq_{\text{surr}} \)

This in turn implies that \( dq_{\text{surr}} \) is independent of how the process in the system occurred, reversible or irreversible. So:

\[
dS_{\text{surr}} = \frac{dq_{\text{surr,rev}}}{T_{\text{surr}}} = \frac{dq_{\text{surr}}}{T_{\text{surr}}}
\]

\( \Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T_{\text{surr}}} \) \( (\text{regardless of how process performed}) \)

So for adiabatic change in the system (no heat transfer with surroundings)

\( \Delta S_{\text{surr}} = 0 \)
7. Show that transfer from a hot to a cold body is spontaneous

\[ dS_{\text{tot}} = dS_1 + dS_2 \]

\[ = \frac{dq}{T_1} - \frac{dq}{T_2} = dq(1/T_1 - 1/T_2) \]

\[ \Delta S_{\text{tot}} = q(1/T_1 - 1/T_2) > 0 \]

B. Entropy changes in specific processes.

1. Isothermal expansion of an ideal gas: have already shown that, no matter how conducted (rev or irrev)

\[ \Delta S = nR \ln \frac{V_2}{V_1} \]

2. Phase Transition at the Transition temperature.

Applies, e.g. to vap, fusion, etc.

System

\[ \Delta S_{\text{trans}} = \Delta H_{\text{trans}}/T_{\text{trans}} \]

trans = vap, fus, etc.

### Standard entropies of phase transitions, \( \Delta_{\text{trs}}S^0/(J \text{ K}^{-1} \text{mol}^{-1}) \)

<table>
<thead>
<tr>
<th></th>
<th>Fusion (at ( T_f ))</th>
<th>Vaporization (at ( T_v ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argon, Ar</td>
<td>14.17 (at 83.8 K)</td>
<td>74.53 (at 87.3 K)</td>
</tr>
<tr>
<td>Benzene, ( \text{C}_6\text{H}_6 )</td>
<td>38.00 (at 279 K)</td>
<td>87.19 (at 353 K)</td>
</tr>
<tr>
<td>Water, ( \text{H}_2\text{O} )</td>
<td>22.00 (at 273.15 K)</td>
<td>109.0 (at 373.15 K)</td>
</tr>
<tr>
<td>Helium, He</td>
<td>4.8 (at 8 K and 30 bar)</td>
<td>19.9 (at 4.22 K)</td>
</tr>
</tbody>
</table>

* More values are given in the Data section.
Problem: The molar enthalpies of vaporization of Cl₂ and benzene are 20.41 and 30.8 kJ/mol, respectively, and their boiling points are 239.1 and 353.2K, respectively. Calculate $\Delta S_{vap}$ in J K⁻¹mol⁻¹ for both.

Cl₂:
$\Delta S_{vap} = (20.41\text{kJ/mol})/239.1\text{K} = 85.36 \text{J/Kmol}$

C₆H₆:
$\Delta S_{vap} = (30.8 \text{kJ/mol})/353.2\text{K} = 87.2 \text{J/K mol}$

Hmmm! Almost identical!

Trouton’s rule: (a general observation)

$\Delta S_{vap} \approx 85 \text{ J K}^{-1}\text{mol}^{-1}$ for most liquids.

Microscopic reason: change in degrees of freedom (W) going from liquid to gas is comparable for most liquids.

Slightly more for well-ordered liquids vaporizing, like H₂O(l) with its H-bonding network.
$\Delta S_{vap}(\text{H}_2\text{O}) = 109.1 \text{ J K}^{-1}\text{mol}^{-1}$

Why larger?

Can use Trouton’s Rule to estimate $\Delta H_{vap}$ from boiling point of the liquid:
$\Delta H_{vap} \approx T_b \times 85 \text{ J K}^{-1}\text{mol}^{-1}$

Just an estimate.

The standard entropies of vaporization of liquids

<table>
<thead>
<tr>
<th>$\Delta_{vap}H^0$/kJ mol⁻¹</th>
<th>$\theta_b$/°C</th>
<th>$\Delta_{vap}S^o$/J K⁻¹mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>30.8</td>
<td>80.1</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>30</td>
<td>76.7</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>30.1</td>
<td>80.7</td>
</tr>
<tr>
<td>Hydrogen sulfide</td>
<td>18.7</td>
<td>−60.4</td>
</tr>
<tr>
<td>Methane</td>
<td>8.18</td>
<td>−161.5</td>
</tr>
<tr>
<td>Water</td>
<td>40.7</td>
<td>100.0</td>
</tr>
</tbody>
</table>

* More values are given in the Data section.
3. Entropy change of heating a system at constant pressure (i.e., the usual scenario):

Always true that $\Delta S = \int_1^2 \frac{dq_{rev}}{T}$

Since constant $p$, $dq_{rev} = C_p dT$

Therefore, $\Delta S = \int C_p dT / T$ (at constant $V$, put in $C_V$)

Over a short $T$ range, assuming $C_p$ is $T$-independent.

$S(T_2) = S(T_1) + C_p \int_{T_1}^{T_2} \frac{dT}{T}$

$= S(T_1) + C_p \ln \frac{T_2}{T_1}$

Can also use these integrations to calculate the absolute entropy $S(T)$ of a substance at a given $T$. Start integrating at $T = 0$.

$S(T) = S(T = 0) + \int_0^{T_f} C_p(\text{solid})/T(dT) + \Delta H_{\text{fus}} / T_f + \int_{T_f}^{T_b} C_p(\text{liq})/T(dT) + \Delta H_{\text{vap}} / T + \int_{T_b}^T C_p(\text{gas})/T(dT)$

First integral has problems, because $C_p(\text{solid})$ may not be known at $T$ near 0 K.

Use Debye theoretical formula $C_p = aT^3$ near $T = 0$. 

![Figure 3-14](Atkins Physical Chemistry, Eighth Edition © 2006 Peter Atkins and Julio de Paula)
C. The Third Law.

1. Third law establishes what is the zero-point entropy, \( S(T=0 \text{ K}) \).

2. Based on Nernst heat theorem: entropy changes of process occurring near \( T = 0 \) are approaching zero.

\[
\Delta S \to 0 \text{ as } T \to 0 \text{ K.}
\]

Implication: \( S \) of all substances at \( T = 0 \) K are about the same.

3. Third law states: \( S \) of all perfect crystalline substances, whether elements or compounds, are equal at \( T = 0 \) K.

4. For convenience, choose \( S=0 \) (at \( T=0K \)) for perfect crystalline substance.

5. This matches Boltzmann formula:

\[
S = k_B \ln W
\]

\( W = 1 \) for perfect crystal at 0 K (only one arrangement) no thermal motion

\[
S = k_B \ln 1 = k \times 0 = 0
\]

6. Any disorder in crystals raises \( S \).

7. Note: some substances have a residual entropy at 0 K.

**Synoptic Table 3B.1**  
Standard Third-Law molar entropies at 298 K

\( S^o_m/(J \text{ K}^{-1} \text{ mol}^{-1}) \)

<table>
<thead>
<tr>
<th>Solids</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite, C(s)</td>
<td>5.7</td>
</tr>
<tr>
<td>Diamond, C(s)</td>
<td>2.4</td>
</tr>
<tr>
<td>Sucrose, C\text{\textsubscript{12}}H\text{\textsubscript{22}}O\text{\textsubscript{11}}(s)</td>
<td>360.2</td>
</tr>
<tr>
<td>Iodine, I\text{\textsubscript{2}}(s)</td>
<td>116.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Liquids</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene, C\text{\textsubscript{6}}H\text{\textsubscript{6}}(l)</td>
<td>173.3</td>
</tr>
<tr>
<td>Water, H\text{\textsubscript{2}}O(l)</td>
<td>69.9</td>
</tr>
<tr>
<td>Mercury, Hg(l)</td>
<td>76.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Gases</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane, CH\text{\textsubscript{4}}(g)</td>
<td>186.3</td>
</tr>
<tr>
<td>Carbon dioxide, CO\text{\textsubscript{2}}(g)</td>
<td>213.7</td>
</tr>
<tr>
<td>Hydrogen, H\text{\textsubscript{2}}(g)</td>
<td>130.7</td>
</tr>
<tr>
<td>Helium, He</td>
<td>126.2</td>
</tr>
<tr>
<td>Ammonia, NH\text{\textsubscript{3}}(g)</td>
<td>126.2</td>
</tr>
</tbody>
</table>

* More values are given in the Data section.
8. We can use tabulated third-law standard state entropies to calculate the entropy change of chemical reactions and physical processes.

\[ \Delta S_{rx}^o = \sum_{\text{products}} \nu S_{m}^o - \sum_{\text{reactants}} \nu S_{m}^o \]

D. Efficiencies of Thermal Processes.

1. Efficiency of heat engines (device for converting heat into work):

   a. Need to first compute maximum work possible. Heat engines work by converting a portion of the heat flow from a hot to cold reservoir into work.

   \[ \Delta S = \Delta S_h + \Delta S_c \]
   \[ \Delta S = |q_c|/T_c - |q_h|/T_h \text{  (must be > 0)} \]

   Therefore, must require \(|q_c| > |q_h| \times T_c/T_h\)

   \[ |w_{\text{max}}| = \text{useable energy (converted to work)} \]
   \[ = |q_h| - |q_c| \]
   \[ \uparrow = |q_h| \times T_c/T_h \]

   \[ |w_{\text{max}}| = |q_h| \times (1 - T_c/T_h) \]

   b. Now, efficiency \(\varepsilon\) is defined as

   \[ \varepsilon = \frac{\text{max work}}{\text{heat flow out of hot body}} = \frac{|w_{\text{max}}|}{|q_h|} \]

   \[ \varepsilon = 1 - T_c/T_h \]

   c. Note that most efficient conditions are when:

   \(T_h \gg T_c\)

   \(\varepsilon = 1\) only if \(T_c = 0\text{K}\) or \(T_h = \infty\text{K}\).
2. The Carnot engine (Ideal gas, 4 steps, all reversible):

A → B isothermal reversible expansion
\[ w = -nRT_h \ln \frac{V_B}{V_A} \]
\[ q = -w \quad \text{(since } dU=0) \]

B → C adiabatic reversible expansion
\[ w = -C_V(T_h - T_c) \]
\[ q = 0 \]

C → D isothermal reversible compression
\[ w = -nRT_c \ln \frac{V_D}{V_C} \]
\[ q = -w \]

D → A adiabatic reversible compression
\[ w = -C_V(T_c - T_h) \]
\[ q = 0 \]

Since all steps reversible (or since S is state function)
\[ \Delta S_{ABCD} = 0 \quad \text{(around a closed loop)} \]

\[ \Delta S_{ABCD} = nR \ln \frac{V_B}{V_A} + 0 + nR \ln \frac{V_D}{V_C} + 0 \]
\[ \text{AB BC CD DA} \]
\[ = nR \ln \frac{V_B V_D}{V_A V_C} = 0 \]
\[ \uparrow = 1 \]

Total work done by engine:
\[ |w| = +nRT_h \ln \frac{V_B}{V_A} + C_V(T_h - T_c) + nRT_c \ln \frac{V_D}{V_C} + C_V(T_c - T_h) \]
Max work achieved when all steps reversible, but to achieve this engine must run infinitesimally slowly, and so is of little value.

3. Refrigerator:
   a. Is a heat engine operating in reverse.
   
   Instead of generating work as heat flows from hot to cold, work is input to get heat to flow from cold to hot.
   
   ![Diagram](image)

   **not feasible**

   **feasible**

   b. Coefficient of performance c:

   \[ c = \frac{|q_c|}{|w|} = \text{heat flow out of the refri} \text{g insides/work required to draw it out} \]

   c. Ideal refrigerator has coefficient \( c^0 \).

   \[ c^0 = \frac{T_c}{(T_h - T_c)} \]

   This is refrigerator operating reversibly.

   Note: performance is diminished as \( T_h - T_c \) gets larger.

   A practical working refrigerator cannot work reversibly because it would be too slow and have lower c value.

4. Heat Pumps:

   Like an inside out refrigerator, gathers heat out of the outdoors which is already at a lower T than the indoors.

   \[ c \approx 5 \text{ for commercial heat pumps} \]
II. Second Law in terms of system variables only.

A. Free energy.

1. 2nd Law states $\Delta S_{\text{tot}} > 0$. This is not always convenient because we must keep track of what's happening in the surroundings.

2. Develop a restatement of 2nd Law written in terms of system variables only.

3. Result: for processes at constant $p$, useful to define:

   Gibbs free energy $G = H - TS$

   “free” means free to do work

   Then, for constant $p$ & $T$ process

   $dG = dH - TdS$

   or $\Delta G = \Delta H - T\Delta S$

   Now we restate 2$^{nd}$ Law: a process is spontaneous if:

   $\Delta G < 0$ (at constant $p$ and $T$)

   Thus, spontaneous processes will be downhill in $G$.

   So now we see there are two factors involved in spontaneity:

   system $\Delta H$ and system $\Delta S$

   Example: system $\Delta S$ of a spontaneous process could actually be negative, but only if $\Delta H$ is negative (exothermic) enough to outweigh $T\Delta S$ term.

   That process would be energetically favorable but entropically unfavorable from a system viewpoint.

   By same token:

   Process could be endothermic (uphill in H) ($\Delta H > 0$) and still be spontaneous if $T\Delta S$ is larger and positive. This explains how endothermic reactions can still be spontaneous.

   These process are said to be entropically driven.

   Summary:

   $\Delta G = \Delta H - T\Delta S$

   spontaneity fct. = energetic aspect - entropic aspect
4. For processes at constant $V$, useful to define:

Helmholtz free energy $A = U - TS$

Then, for a const $V$ and $T$ process

$$dA = dU - TdS$$

$$\Delta A = \Delta U - T\Delta S$$

Same meaning as for $\Delta G$, but constant $V$ & $T$ conditions.

5. Interpretation of $\Delta A$ as Maximum Work possible:

$$dw_{max} = dA$$

$$w_{max} = \Delta A$$

$|\Delta A|$ is maximum work than be derived from process when internal energy expended is $|\Delta U|$.

$-T\Delta S$ can be thought of as the “heat tax” imposed by nature.

6. Interpretation of $\Delta G$ as the maximum non-expansion work (or additional work) possible.

This would be work like passing ions across a cell membrane in biology, or passage of electrons in an electrochemical cell.

$$dw_{add,max} = dG$$

$$w_{add,max} = \Delta G$$

7. Standard Reaction Gibbs energies can be calculated from enthalpies and entropies:

$$\Delta G_r^o = \Delta H_r^o - T\Delta S_r^o$$

and standard Gibbs energies of formation can be tabulated and then used to find Gibbs energies of reactions as:

$$\Delta G_r^o = \sum_{products} v\Delta G_f^o - \sum_{reactants} v\Delta G_f^o$$

Synoptic Table 3C.1* Standard Gibbs energies of formation (298 K) $\Delta G^o/(\text{kJ mol}^{-1})$

<table>
<thead>
<tr>
<th>Substance</th>
<th>$\Delta G_f^o$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamond, C(s)</td>
<td>+2.9</td>
</tr>
<tr>
<td>Benzene, C$_6$H$_5$(l)</td>
<td>+124.3</td>
</tr>
<tr>
<td>Methane, CH$_4$(g)</td>
<td>-50.7</td>
</tr>
<tr>
<td>Carbon dioxide, CO$_2$(g)</td>
<td>-394.4</td>
</tr>
<tr>
<td>Water, H$_2$O(l)</td>
<td>-237.1</td>
</tr>
<tr>
<td>Ammonia, NH$_3$(g)</td>
<td>-16.5</td>
</tr>
<tr>
<td>Sodium chloride, NaCl(s)</td>
<td>-384.1</td>
</tr>
</tbody>
</table>
B. Combined 1st and 2nd Law:

1. Derive the **fundamental equation**:

\[
\begin{align*}
\text{d}U &= \text{dq} + \text{dw} \\
\text{reversible} &\quad \text{reversible} \\
T \text{S} &\quad -p \text{d}V \\
\text{d}U &= \text{dq} + \text{dw} \\
\text{irreversible} &\quad \text{irreversible} \\
(T \text{d}S - \delta) &\quad (-p \text{d}V - \delta) \\
\text{cancel}
\end{align*}
\]

So \( \text{d}U = T \text{d}S - p \text{d}V \) regardless of reversible or irreversible; only requirement is that of closed system (no matter flow)

**\[ \text{d}U = T \text{d}S - p \text{d}V \]**

2. Can now make other identifications:

Since \( U \) = function of \( S \) and \( V \), write:

\[
\text{d}U = (\partial U / \partial S)_V \text{d}S + (\partial U / \partial V)_S \text{d}V
\]

\[
\uparrow \quad \uparrow \quad T \quad -p \quad \text{(comparing term by term with above)}
\]

Now we have completely thermodynamic (non-statistical) definition of \( T \):

\[
T = (\partial U / \partial S)_V
\]

3. Properties of the Gibbs energy:

\[
\text{d}G = \text{d}(H - TS)
\]

\[
= \text{d}H - T \text{d}S - S \text{dT}
\]

\[
\uparrow \text{d}(U + pV) \\
\uparrow \text{d}U + p \text{d}V + V \text{d}p
\]

\[
\text{d}G = \text{d}U + p \text{d}V + V \text{d}p - T \text{d}S - S \text{dT}
\]

\[
\uparrow \quad \quad \uparrow \quad \quad - \text{d}U
\]

\[
= V \text{d}p - S \text{dT}
\]
\[ dG = Vdp - SdT \]

Implications: \( G \downarrow \) as \( T \uparrow \) since \( S \) always \( > 0 \).

\( G \uparrow \) as \( p \uparrow \) since \( V \) always \( > 0 \).

Viewing \( G \) as a function of \( p \) and \( T \):

\[ dG = \left( \frac{\partial G}{\partial p} \right)_T dp + \left( \frac{\partial G}{\partial T} \right)_p dT \]

\( V \uparrow \) \( -S \)

Comparing with previous equation

Now we're ready to establish the \( T \) and \( p \) dependence of \( G \).

4. Temperature dependence of \( G \):

Important because it will later show us how the equilibrium constant \( K_{eq} \) of a reaction depends on \( T \).

\[ \left( \frac{\partial G}{\partial T} \right)_p = -S \quad \text{from above; see graph at right} \]

\[ = -\left( \frac{H - G}{T} \right) \]

\[ \left( \frac{\partial G}{\partial T} \right)_p - \frac{G}{T} = -\frac{H}{T} \]

\[ T \left( \frac{\partial \left( G/T \right)}{\partial T} \right)_p = -\frac{H}{T} \quad \text{using product rule of diff} \]

so we obtain **Gibbs-Helmholtz Equation**:

\[ \left( \frac{\partial \left( G/T \right)}{\partial T} \right)_p = -\frac{H}{T^2} \]

or for whole processes, such as chemical reaction:

\[ \left( \frac{\partial \left( \Delta G/T \right)}{\partial T} \right)_p = -\frac{\Delta H}{T^2} \quad \text{(constant \( T \) & \( p \))} \]

Important thing to notice: \( \Delta G \) dependence on \( T \) depends on the enthalpy of reaction.
For example: endothermic rxn has positive $\Delta H$.

Therefore, $\Delta G/T \downarrow$ as $T \uparrow$  
spontaneity $\uparrow$ as $T \uparrow$

$K_{eq} \uparrow$ as $T \uparrow$

Will see later that

$$K_{eq} = e^{-\Delta G^0/RT}$$

$$\Delta G^0 = -RT \ln K_{eq}$$

5. Pressure dependence of $G$:

Let's study this at fixed $T$

$$dG = V dp - SdT$$

$$\uparrow = 0$$

$$G_f - G_i = \int_{p_i}^{p_f} V dp$$

For solid and liquids, since $V$ changes very slightly with pressure:

$$G_f - G_i \approx V \int_{p_i}^{p_f} dp = V \Delta p \approx \text{very small since } V \text{ small.}$$

Implies $\Delta G_{\text{rxn}}$ very weakly $p$-dependent for solids and liquids.

For gases, however:

$$G_f - G_i = \int_{p_i}^{p_f} \left(\frac{nRT}{p}\right) dp \quad \text{(perfect gas)}$$

$$G_f - G_i = nRT \ln p_f/p_i$$

Or in terms of molar Gibbs energies $G_m$:

$$G_m(p_f) - G_m(p_i) = RT \ln p_f/p_i$$
Implies $\Delta G_{\text{rxn}}$ more strongly $p$-dependent for rxns involving gases.

$$0 = RT \ln \frac{p_2}{p_1} + \Delta G_{\text{rxn}}(p_2) - 2RT \ln \frac{p_2}{p_1} - \Delta G_{\text{rxn}}(p_1)$$

$$\Delta G_{\text{rxn}}(p_2) = \Delta G_{\text{rxn}}(p_1) + (2-1)RT \ln \frac{p_2}{p_1}$$

$$\Delta G_{\text{rxn}}(p_2) = \Delta G_{\text{rxn}}(p_1) + (\Delta n_{\text{g}})RT \ln \frac{p_2}{p_1}$$

$\Delta n_{\text{g}} = \text{change in gas moles}$

6. Relate Gibbs energy of a gas to the standard state Gibbs energy:

Since $G_m(p_2) = G_m(p_1) + RT \ln \frac{p_2}{p_1}$

if $p_1 = 1 \text{ bar (standard pressure)} = p$,

$p_2 = \text{our working pressure } p$

$$G_m(p) = G_m^\circ + RT \ln \frac{p}{p^0}$$

This is a very important statement when we begin to discuss chemical equilibrium, because of the relation of the equilibrium constant to the reaction quotient of gas pressures.

$$K_{\text{eq}} = \frac{p_{\text{NO}_2}^2}{p_{\text{N}_2\text{O}_4}}$$